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Interfacial and Thermodynamic Properties of Aqueous HCl + Cetyltrimethylammonium Chlorine + Alkanol + Diesel Oil Microemulsion: Effect of HCl in the Aqueous Phase

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The interfacial and thermodynamic properties of aqueous HCl + cetyltrimethylammonium chlorine (CTAC) + alkanol + diesel oil w/o microemulsion systems were investigated by the method of dilution. Aqueous hydrochloric acid solution (mass fraction 20 %) was used to investigate the effect of HCl on the formation of microemulsion. The composition of the cosurfactant and the surfactant in the interfacial region, the distribution of the cosurfactant between the interfacial region and the continuous oil phase, the energetics of transfer of the cosurfactant from the oil to the interface, and the structural parameters of the microemulsion were estimated at (303, 313, and 323) K.

Introduction

Microemulsions are isotropic, transparent, and thermodynamically stable systems composed of water, oil, surfactant, and cosurfactant. Traditionally, microemulsions have been considered as high potential value in different aspects of crude oil exploitation, such as enhanced oil recovery, acidizing, and gas hydrates.[1] Acidizing is the process where an acid is injected into a well to remove the formation damage from pore plugging caused by deposition of mineral particles and as a result increases the crude oil production.[2,3] To realize the deep acidification and improve the effect of the acidizing operation, the reactivity of the acid with carbonate in the matrix must be reduced. When acid droplets disperse in oil to form microemulsions, the diffusion of the protons and the rate of the diffusion-controlled reaction of the microemulsions will reduce. So, microemulsion with a high concentration of HCl in the water phase is a potential acidizing system. The data of the formation and the structure and thermodynamic properties of microemulsions containing acids are important but have seldom been reported.

To study the structure of w/o microemulsions, the role of the cosurfactant on the stabilization of the interface, the component ratio of the cosurfactant between oil phase and the interfacial region, along with the thermodynamics of the formation of the interface, a simple but elegant method of dilution has been used by a number of workers.[4–11] The dilution experiment is normally carried out by adding oil at a constant water and surfactant composition to destabilize a stable water/oil microemulsion and then restabilize it by adding a requisite amount of alkanol. The distribution parameters and the relation with thermodynamic parameters can be calculated and analyzed from the dilution method.

In this paper, we describe our study using the dilution method on microemulsified acid systems, using HCl + H_2O as the aqueous phase, diesel oil as the oil phase, cetyltrimethylammonium chloride (CTAC) as the surfactant, and a number of alkanols (1-butanol, 1-pentanol, 2-methyl-1-butanol, 1-hexanol, and 1-octanol) as cosurfactants, at different temperatures. To calculate the structure parameters, the interfacial composition and the thermodynamic parameters, the analytical treatment based on equilibrium thermodynamics proposed by Moulik et al.,[4–8] Bayrak,[9] and Zheng et al.[10,11] was used. The effect of HCl on the above parameters was investigated.

Experimental Section

Materials. Cetyltrimethylammonium chloride (CTAC, purity > 99 %) was obtained from Shanghai Jahwa Company (China). Analytical grade hydrochloric acid was purchased from Sinopharm Chemical Reagent Company, Ltd. The alkanols, 1-butanol, 1-pentanol, 2-methyl-1-butanol, 1-hexanol, and 1-octanol (purity > 99.5 %) were all analytical grade and purchased from Shanghai Defei Chemical Company. The $0^{\#}$ diesel oil was provided by SINOPEC in Shanghai (solidifying point 0 °C, density 8.41 $g \cdot mL^{-3}$, Mn = (220 to 240) $g \cdot mol^{-1}$). All these chemicals were used without further purification. Distilled water was used in the experiments.

Dilution Experiments. In the dilution experiments, a fixed amount of surfactant (approximately $7.2 \cdot 10^{-4}$ mol of CTAC) was added to a dry test tube and mixed with constant amounts of oil (10 mL of the diesel oil) and water or mass fraction of 20 % HCl in H_2O (approximately 0.78 g). The sample was then placed in a thermostatted water bath (temperature control accuracy ± 0.1 K), stirred constantly using a magnetic stirrer, and kept well covered to prevent loss by evaporation. The alkanol was added slowly to the initially turbid mixture from a microsyringe until the solution became just clear at the temperature of the experiment, allowing sufficient time for

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equilibration. The volume of alkanol at that point was noted. At this stage, 5 mL of diesel oil was added to the system to destabilize it. The cloudy solution was then made just clear by the addition of an alkanol; the quantity of alkanol added was also recorded. This procedure was repeated five times, noting the volume of the oil and the alkanol necessary at each step for obtaining a clear and stable w/o microemulsion. The entire procedure was followed at three temperatures, (303, 313, and 323) K, for the alkanols: 1-butanol, 1-pentanol, 2-methyl-1-butanol, 1-hexanol, and 1-octanol. Each set of experiments was repeated two or three times, and the average of the values obtained was used for data processing and analysis.

Results and Discussion

Basics of the Dilution Method. For a quaternary w/o microemulsion system composed of water + surfactant + alkanol (cosurfactant) + oil, the stability is governed by the distribution of the alkanol between oil and the interface at a fixed temperature. The solubility of alkanol in oil was considered to be an invariable constant term K, when a fixed amount of water, oil, and surfactant was used to form a stable w/o microemulsion at a fixed temperature. Increasing the oil content alters the interfacial concentration of the cosurfactant and consequently causes the system to split into two distinct phases. Then adding a sufficient amount of cosurfactant can regain a stable and transparent dispersion and thus reestablish the distribution constant. This process is repeatedly followed in the dilution experiment.[9–15]

The total number of moles of the alkanol cosurfactant n_a present in the stable system is given by the relation

$$n_a = n_a^i + n_a^w + n_a^o \tag{1}$$

where the superscripts w, i, and o stand for the water, interfacial, and oil phase, respectively.

Since the solubility of alkanol in the oil is constant at a given temperature, the constant K can be written as

$$K = \frac{n_a^o}{n_o} \tag{2}$$

where n_a^o and n_o are the number of moles of the alkanol in the oil phase and the total number of moles of oil, respectively.

Combining eq 1 and eq 2 we get

$$n_a = n_a^i + n_a^w + Kn_o \tag{3}$$

Dividing throughout by the total number of moles of surfactant (n_s), eq 3 may be converted into a more convenient form

$$\frac{n_a}{n_s} = \frac{n_a^i + n_a^w}{n_s} + K\frac{n_o}{n_s} \tag{4}$$

Water solubility of alchols can be negligible ($n_a^w \approx 0$, for alkanols higher than butanol), and the above equation becomes

$$\frac{n_a}{n_s} = \frac{n_a^i}{n_s} + K\frac{n_o}{n_s} \tag{5}$$

A plot of n_a/n_s against n_o/n_s should yield the values of the slope (S) and the intercept (I). Slope (S) is actually K, and n_a^o can be determined from eq 2. On the other hand, the intercept (I) is equal to n_a^i/n_s in which n_a^i can be calculated.

The partition of alkanol between the continuous oil phase and the interface of the droplet can be expressed in terms of the distribution constant (K_d). K_d can be calculated from the ratio of the mole fraction of alkanol in the interfacial composition (x_a^i) to the mole fraction of alkanol in the bulk oil phase (x_a^o).

$$K_d = \frac{x_a^i}{x_a^o} = \frac{\dfrac{n_a^i}{n_a^i + n_s}}{\dfrac{n_a^o}{n_a^o + n_o}} = \frac{n_a^i(n_a^o + n_o)}{n_a^o(n_a^i + n_s)} \tag{6}$$

Dividing the numerator and denominator by $n_o n_s$ and putting the values of the slope (S) and the intercept (I) from eq 5, we get

$$K_d = \frac{\dfrac{n_a^i(n_a^o + n_o)}{n_o n_s}}{\dfrac{n_a^o(n_a^i + n_s)}{n_o n_s}} = \frac{\dfrac{n_a^i}{n_s}\left(\dfrac{n_a^o}{n_o} + 1\right)}{\dfrac{n_a^o}{n_o}\left(\dfrac{n_a^i}{n_s} + 1\right)} = \frac{I(S+1)}{S(I+1)} \tag{7}$$

The standard Gibbs free energy of transfer (ΔG_t^o) of alkanol from the oil phase to the interfacial region is obtained from the relation

$$\Delta G_t^o = -RT \ln K_d = -RT \ln \frac{x_a^i}{x_a^o} = -RT \ln \frac{I(S+1)}{S(I+1)} \tag{8}$$

A polynomial fitting between ΔG_t^o and the temperature T is used to obtain ΔS_t^o from its first derivative

$$\left[\frac{\partial(\Delta G_t^o)}{\partial T}\right]_P = -\Delta S_t^o \tag{9}$$

From the knowledge of $\Delta G_t{}^o$ and $\Delta S_t{}^o$, the enthalpy change of the transfer process can be calculated according to the Gibbs–Helmholtz equation

$$\Delta H_t^o = \Delta G_t^o + T\Delta S_t^o \tag{10}$$

The standard state herein considered is the hypothetical ideal state of unit mole fraction.

Interfacial Composition of the Microemulsion. The data collected in the present dilution experiments were constructed by plotting n_a/n_s versus n_o/n_s according to eq 5. Three representative plots at different temperatures were illustrated in Figure 1. The plots were strikingly linear. S and I were obtained from the slope and intercept, respectively. The calculated results were presented in Table 1. In the calculation of I and n_a^i/n_s, the aqueous solubility of 1-butanol at the temperature of measurement was considered. This was ignored for other alkanols because of their negligible aqueous solubilities. It was obvious that both S and I depended on temperature and alkanol carbon chain.

For 1-hexanol, 1-octanol, and 2-methyl-1-butanol, the values of S increased with temperature increase, whereas I decreased. This indicated that the mass of 1-hexanol, 1-octanol, and 2-methyl-1-butanol dissolved in diesel oil increased as temperature increased, whereas an opposite trend was followed in the interfacial region. For 1-butanol and 1-pentanol, the values of S and I did not follow any straightforward trend as temperature increased. At a constant temperature, the values of S and I decreased with an increase in the alkanol carbon number. So, a lower mass of alkanol with longer carbon chain was required to form stable microemulsified acid. In addition, S and I of 1-butanol and 1-pentanol were much greater with HCl in the water phase than with pure water as shown in Table 1. The

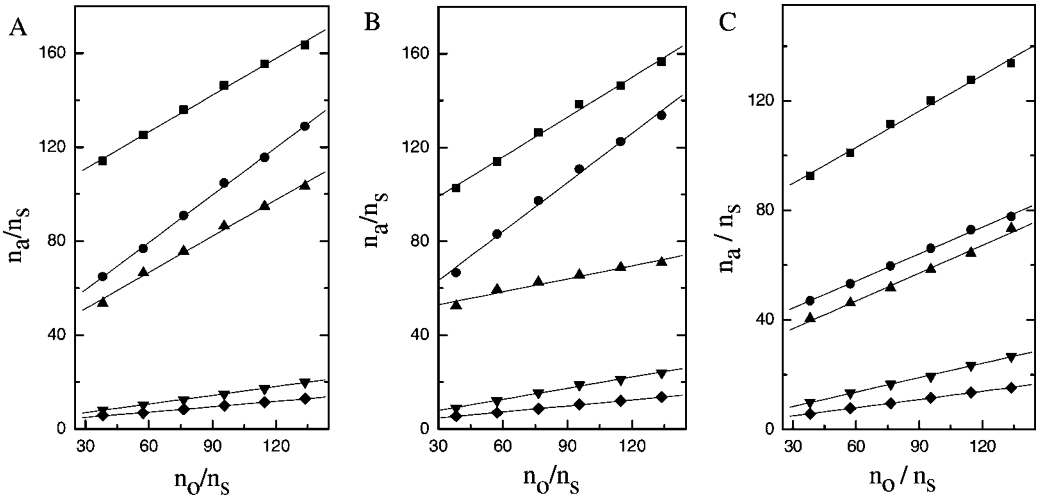

Figure 1. Plot of n_a/n_s vs n_o/n_s according to eq 5 for aqueous HCl + CTAC + alkanol + diesel oil w/o microemulsion systems at 303 K (A), 313 K (B), and 323 K (C). ■, 1-butanol; ●, 1-pentanol; ▲, 2-methyl-1-butanol; ▼, 1-hexanol; ♦, 1-octanol.

Table 1. Interfacial Parameters n_a^o/n_o, n_a^i/n_s, n_s, and n_a^i of the Aqueous HCl + CTAC + Alkanol + Diesel Oil w/o Microemulsion with Different Alkanols at Different Temperatures[a]

cosurfactant	T / K	n_a^o/n_o / HCl (H_2O)	n_a^i/n_s / HCl (H_2O)	$10^4 n_s$ / mol	$10^4 n_a^i$ / mol
1-butanol	303	0.522 (0.871)	94.387 (22.494)	7.198	679.397
	313	0.566 (0.495)	81.294 (32.923)	7.228	587.591
	323	0.440 (0.388)	76.567 (29.059)	7.254	555.419
1-pentanol	303	0.673 (0.311)	39.014 (6.764)	7.223	281.800
	313	0.697 (0.241)	42.334 (5.088)	7.211	305.274
	323	0.329 (0.195)	34.456 (8.650)	7.320	438.440
1-hexanol	303	0.123 (0.258)	3.324 (4.244)	7.272	24.169
	313	0.158 (0.241)	3.218 (5.088)	7.229	23.262
	323	0.174 (0.198)	3.192 (7.226)	7.152	22.826
1-octanol	303	0.076 (0.159)	2.654 (3.337)	7.175	19.041
	313	0.086 (0.177)	2.213 (4.398)	7.231	16.005
	323	0.100 (0.198)	1.960 (4.488)	7.152	14.014
2-methyl-1-butanol	303	0.171 (0.475)	35.743 (10.685)	7.199	257.316
	313	0.185 (0.468)	47.409 (6.743)	7.189	340.822
	323	0.338 (0.207)	26.644 (6.905)	7.191	191.597

[a] Note: 0 values of (0.58, 0.537, and 0.519) mmol for butan-1-ol per 33.80 mmol of water at (303, 313, and 323) K, respectively, were taken in the calculation.[7] The data in parentheses represent the microemulsions with pure water as the water phase. The uncertainty limits of n_a^o/n_o, n_a^i/n_s, and n_a^i are 2 %.

Table 2. Thermodynamic Parameters for Transfer of Alkanol from the Oil Phase to the Interfacial Layer ΔG_t^o, ΔS_t^o, and ΔH_t^o of Aqueous HCl + CTAC + Alkanol + Diesel Oil w/o Microemulsion with Different Alkanols at Different Temperatures[a]

cosurfactant	T / K	ΔS_t^o / $J \cdot K^{-1} \cdot mol^{-1}$	ΔG_t^o / $kJ \cdot mol^{-1}$	ΔH_t^o / $kJ \cdot mol^{-1}$
1-butanol	303	−34.60	−2.67 (−1.82)	−13.15
	313	24.00	−2.62 (−2.80)	4.90
	323	82.60	−3.15 (−3.33)	23.53
1-pentanol	303	68.00	−2.23 (−3.28)	18.37
	313	−72.00	−2.25 (−3.80)	−24.79
	323	−21.20	−3.67 (−4.58)	−10.52
1-hexanol	303	−60.70	−4.92 (−3.46)	−23.31
	313	−26.10	−4.48 (−3.80)	−12.65
	323	8.50	−4.39 (−4.49)	−1.65
1-octanol	303	−18.80	−5.86 (−4.34)	−11.56
	313	−26.00	−5.64 (−4.40)	−13.77
	323	−33.20	−5.34 (−4.29)	−16.06
2-methyl-1-butanol	303	60.00	−4.77 (−2.63)	13.41
	313	−59.00	−4.78 (−2.62)	−23.25
	323	−178.80	−3.59 (−4.37)	−61.35

[a] Note: The data in parentheses represent the microemulsion with pure water as the water phase. The uncertainty limits of ΔG_t^o, ΔH_t^o, and ΔS_t^o are ± 3 %, ± 5 %, and ± 8 %, respectively.

number of moles of 1-butanol and 1-pentanol in the oil phase (n_a^o) and in the interfacial phase (n_a^i) were all considerably higher than other alkanols. This showed that to form a stable aqueous HCl + CTAC + alkanol + diesel oil microemulsion, an additional amount of 1-butanol and 1-pentanol was required. For microemulsions formed by 1-hexanol and 1-octanol as cosurfactants, *S* and *I* were smaller with HCl in the water phase than with pure water, which indicated that adding a smaller amount of 1-hexanol and 1-octanol can obtain a stable microemulsified acid system.

Thermodynamics of Transfer of Alkanols to the Interface. In the thermodynamic calculations, ideal behavior was assumed, and the concentration was expressed on the mole fraction scale. The standard Gibbs free energy of transfer (ΔG_t^o) of the alkanol from the continuous oil phase to the interfacial region, between the water and oil, at the studied temperatures was obtained from eq 8. The standard entropy change (ΔS_t^o) of the transfer process was obtained from the first derivative of a polynomial fitting between ΔG_t^o and temperature (T), according to eq 9. Then the enthalpy change (ΔH_t^o) of the transfer process was calculated according to the Gibbs−Helmholtz equation (eq 10).

The thermodynamic parameters for all the alkanols are presented in Table 2. The results revealed that the ΔG_t^o value for all the alkanols was negative at experimental temperature. Consequently, the HCl + CTAC + alkanol + diesel oil microemulsion forms spontaneously no matter which alkanol is used as the cosurfactant. In comparison, the ΔG_t^o values of 1-octanol

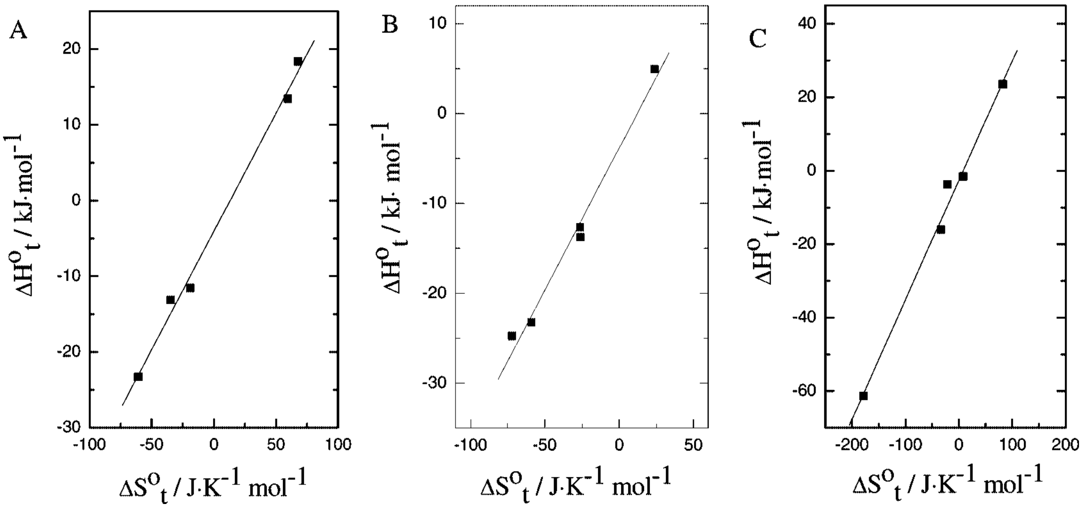

Figure 2. Enthalpy−entropy compensation plots for aqueous HCl + CTAC + alkanol + diesel oil microemulsion systems at different temperatures: (A) 303 K, corresponding compensation temperatures $T_{\mathrm{comp}} = 311$ K; (B) 313 K, corresponding compensation temperatures $T_{\mathrm{comp}} = 316$ K; (C) 323 K, corresponding compensation temperatures $T_{\mathrm{comp}} = 325$ K.

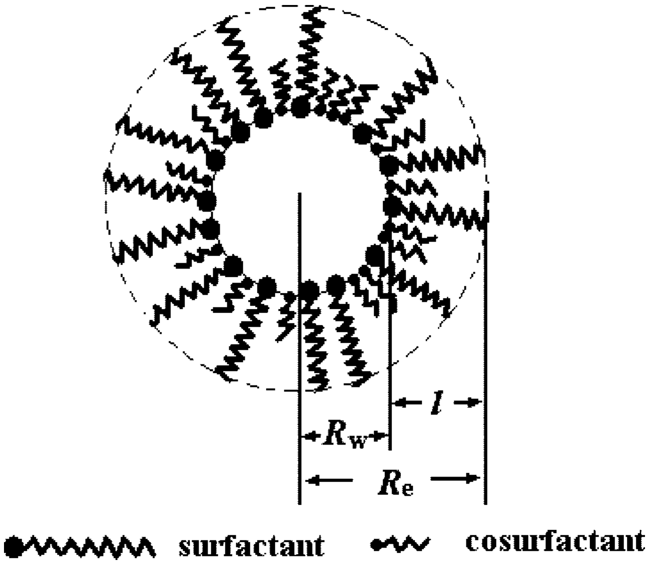

Figure 3. Sketch structure of w/o microemulsion: R_w, the radius of the water pool; R_e, the effective radius including the interface; l, the thickness of the interfacial layer including surfactant and cosurfactant.

were the most negative, and the transfer process of 1-octanol was to some extent more spontaneous than other alkanols. Otherwise, the ΔG_t^o values of 1-octanol for HCl + CTAC + alkanol + diesel oil microemulsion are more negative compared with H_2O + CTAC + alkanol + diesel oil microemulsion, so the transfer of 1-octanol from oil to interface is more favorable when using aqueous HCl. The ΔH_t^o values are mostly negative which shows that the process is exothermic and the transfer process of alkanols from oil to the interface releases heat. The ΔS_t^o values varied, being both positive and negative for all alkanols. The microemulsion forming systems can end up in both more ordered and more disordered states, depending on their chemical composition and the thermal condition. The negative entropic change was due to the better organization of the interface and its surroundings. The interface composed by 1-octanol and CTAC became more ordered at all three experimental temperatures, as the parameters reported in Table 2.

In kinetics and equilibrium studies, an extra-thermodynamic correlation between the enthalpic and the entropic changes for the involved process is often reported, called the enthalpy−entropy compensation effect. Micelle and microemulsion systems often obey the extra thermodynamic linear correlation between the enthalpic and entropic changes.[4,7,12–14] The thermodynamic results for HCl + CTAC + alkanol + diesel oil microemulsion were collected and tested for this correlation and are illustrated in Figure 2. Good linear correlations were observed at the three temperatures. Thus, microemulsions with a high content of hydrochloric acid also obey the extra thermodynamic linear correlation between the enthalpic and entropic changes. The linear correlation suggests mutual adjustment between the total enthalpy and the entropy during the alkanol transfer process. The compensation temperatures (T_{comp}) were (311, 316, and 325) K vis-à-vis the experimental temperatures (303, 313, and 323) K, respectively. Such a deviation of the compensation temperature from the experimental temperature is not uncommon in the literature for microemulsion systems.[4,7,12–14] The highly linear correlation for $\Delta H_t^o - \Delta S_t^o$ is due to the propagation of experimental error which emanates from the fact that these thermodynamic parameters are usually derived over a very short range of $1/T$, which are far from the origin.[7] Thus, the compensation temperature usually comes out to be in close proximity to the experimental temperatures.

Structure Parameters of the Microemulsion. The droplets of the w/o microemulsion are assumed to be spherical and monodisperse and with a surface monolayer composed of surfactant and cosurfactant molecules as shown in Figure 3. The following relation represents the total volume of the droplets (V_d)

$$V_d = \frac{4}{3}\pi R_e^3 N_d \tag{11}$$

where R_e and N_d are the effective radius (including the interface) and the total number of droplets in the microemulsion sample, respectively. V_d can also be calculated from another point of view. It is equal to the sum of the volumes of water V_{H_2O}, surfactant V_s, and cosurfactant alkanol V_a^i at the interface

$$V_d = V_{H_2O} + V_s + V_a^i \tag{12}$$

When the water phase contains HCl, the V_{H_2O} includes the volume of HCl (V_{HCl}). V_{HCl} is estimated in terms of the contributions of V_H and V_{Cl}. The V_H and V_{Cl} can be estimated

Table 3. Structural Parameters R_w, R_e, l, and N_d of Aqueous HCl + CTAC + Alkanol + Diesel Oil Microemulsions and H_2O + CTAC + Alkanol + Diesel Oil Microemulsions with Different Alkanols at a Constant Water Content but at Different Temperatures

		R_w		R_e		l			
	T	nm		nm		nm		N_d	
cosurfactant	K	HCl	H_2O	HCl	H_2O	HCl	H_2O	HCl	H_2O
1-butanol	303	0.25	1.07	0.55	1.59	0.30	0.53	$10.28 \cdot 10^{21}$	$1.50 \cdot 10^{20}$
	313	0.29	0.74	0.61	1.20	0.32	0.46	$6.71 \cdot 10^{21}$	$4.56 \cdot 10^{20}$
	323	0.31	0.84	0.63	1.33	0.32	0.49	$5.69 \cdot 10^{21}$	$3.03 \cdot 10^{20}$
1-pentanol	303	0.60	3.07	1.07	3.90	0.47	0.83	$7.92 \cdot 10^{20}$	$6.26 \cdot 10^{18}$
	313	0.55	3.80	1.01	4.70	0.46	0.89	$9.97 \cdot 10^{20}$	$3.30 \cdot 10^{18}$
	323	0.39	2.48	0.78	3.25	0.39	0.78	$28.51 \cdot 10^{20}$	$1.19 \cdot 10^{19}$
1-hexanol	303	4.76	4.38	5.81	5.39	1.05	1.00	$1.56 \cdot 10^{18}$	$2.15 \cdot 10^{18}$
	313	4.89	3.84	5.95	4.80	1.06	0.96	$1.44 \cdot 10^{18}$	$3.22 \cdot 10^{18}$
	323	4.97	2.85	6.03	3.73	1.06	0.88	$1.37 \cdot 10^{18}$	$7.83 \cdot 10^{18}$
1-octanol	303	5.56	5.07	6.77	6.24	1.21	1.17	$9.79 \cdot 10^{17}$	$1.40 \cdot 10^{18}$
	313	6.13	4.21	7.38	5.32	1.24	1.12	$7.30 \cdot 10^{17}$	$2.44 \cdot 10^{18}$
	323	6.63	4.11	7.89	5.22	1.26	1.11	$5.79 \cdot 10^{17}$	$2.61 \cdot 10^{18}$
2-methyl-1-butanol	303	0.65	2.07	1.14	2.81	0.49	0.73	$6.10 \cdot 10^{20}$	$2.03 \cdot 10^{19}$
	313	0.50	3.03	0.93	3.86	0.43	0.83	$13.70 \cdot 10^{20}$	$6.54 \cdot 10^{18}$
	323	0.86	3.01	1.40	3.84	0.54	0.83	$2.64 \cdot 10^{20}$	$6.64 \cdot 10^{18}$

from the radius of H and Cl, which are (0.12 and 0.18) nm, respectively.[15]

$$V_{HCl} = (V_H + V_{Cl}) n_{HCl} N_A \tag{13}$$

where N_A is the Avogadro constant.

V_a^i can be obtained from the dilution experiment

$$V_a^i = \frac{n_a^i M_a}{\rho_a} = \frac{I n_s M_a}{\rho_a} \tag{14}$$

where M_a and ρ_a are the molar mass and the density of alkanol, respectively. The V_s is estimated in terms of the contributions of various groups: the volumes of tail, V_{tail}, and of head, V_{head}, per surfactant molecule

$$V_s = (V_{tail} + V_{head}) n_s N_A \tag{15}$$

where V_{CTAC} is 0.616 nm^3, V_{tail} of CTAC is 0.459 nm^3, and V_{head} of CTAC is 0.157 nm^3.[16]

Since the surfactant and alkanol are considered to pack closely on the surface of the water pool, the total sectional area of the surfactant and alkanol occupied equal approximately the total surface area of the water pool

$$(n_s A_s + n_a^i A_a) N_A = (A_s + I A_a) n_s N_A = 4\pi R_w^2 N_d \tag{16}$$

and

$$R_w = 3 V_{H_2O} / (A_s + I A_a) n_s N_A \tag{17}$$

where A_s and A_a are the sectional areas of the headgroup of the surfactant and alkanol, respectively. R_w is the radius of the water pool. The effective value of A_s can be estimated from the V_{head}, which is 0.35 nm^2. The value of A_a is 0.20 nm^2 for alkanol.[5] Thus, R_e is obtained from the relation

$$R_e = R_w \sqrt[3]{\frac{V_d}{V_{H_2O}}} \tag{18}$$

Putting the values of R_e and V_d into eq 11, we get the value of N_d. Thus, the effective thickness of the interfacial layer of droplet l also follows

$$l = R_e - R_w \tag{19}$$

The structural parameters of the aqueous HCl + CTAC + alkanol + diesel oil microemulsions and H_2O + CTAC + alkanol + diesel oil microemulsions, such as R_w, R_e, l, and N_d, were calculated according to eqs 11 to 19, and the data were listed in Table 3. Comparing structural parameters of the two microemulsion systems, with high content of HCl in water pool, the R_w and R_e in aqueous HCl + CTAC + alkanol + diesel oil microemulsions with 1-hexanol, 1-octanol, and 2-methyl-1-butanol as cosurfactants were obviously smaller than that in H_2O + CTAC + alkanol + diesel oil microemulsions. This led to the number of the droplets N_d in the former being much larger than that in the latter at the same temperature. This supported the above Table 1, and the surfaces of a larger number of droplets in aqueous HCl + CTAC + alkanol + diesel oil microemulsions needed more 1-hexanol, 1-octanol, and 2-methyl-1-butanol as cosurfactants. Moreover, the effective thickness of the interfacial layer of droplet l in the former was also smaller than that in the latter. Obviously, the increase in the content of the alkanols at the interfacial layer will reduce l since the carbon chain length of alkanols is much shorter than that of CTAC. But for 1-hexanol and 1-octanol, the R_w and R_e in aqueous HCl + CTAC + alkanol + diesel oil microemulsions were larger than those in H_2O + CTAC + alkanol + diesel oil microemulsions. The N_d values decreased in aqueous HCl + CTAC + alkanol + diesel oil microemulsions, which followed the varying tendency of R_w and R_e. Consequently, a smaller amount of 1-hexanol and 1-octanol was required for aqueous HCl + CTAC + alkanol + diesel oil microemulsions than for H_2O + CTAC + alkanol + diesel oil microemulsions. l showed an increase with amount of 1-hexanol and 1-octanol decreasing in the interfacial region, which was consistent with the above discussion in Table 1.

Conclusions

The dilution method for the understanding of the interfacial composition, thermodynamic parameters, and structural parameters of aqueous HCl + CTAC + alkanol + diesel oil microemulsions has been found to be reasonable. The high content of HCl in the water phase causes all the parameters to change and vary according to different trends with temperature and alkanol carbon chain. Compared with H_2O + CTAC + alkanol + diesel oil microemulsions, a larger amount of 1-butanol, 1-pentanol, and 2-methyl-1-butanol is required to form aqueous HCl + CTAC + alkanol + diesel oil microemulsions. A larger number of water droplets with HCl (N_d) form, and the acid droplets become smaller. Whereas, a smaller amount of 1-hexanol and 1-octanol is needed to form microemulsions with HCl in the water pool, the acid droplets become larger and the number of droplets decreases. The ΔG_t^o values of the alkanol transfer process are all negative, and the value is most negative for 1-octanol. The enthalpy of the process is mostly exothermic. The ΔS_t^o values of 1-octanol are all negative at three experimental temperatures. It is implied that to form stable aqueous HCl + CTAC + alkanol + diesel oil w/o microemulsion 1-octanol as cosurfactant is a more suitable cosurfactant than others.

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